Highly active and reusable palladium nanoparticle catalyst stabilized by polydimethylsiloxane for hydrogenation of aromatic compounds in supercritical carbon dioxide

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ARTICLE INFO

ABSTRACT

This study describes a hydrogenation method for degrading polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in supercritical carbon dioxide catalyzed by palladium nanoparticles stabilized in polydimethylsiloxane (Pd/PDMS). The process of synthesizing metal nanoparticles embedded in PDMS polymers involves the preparation of a homogenous mixture of metal salt, silicone elastomer, and a curing agent, followed by hydrogen reduction. PCBs and PAHs can be effectively hydrogenated to saturated hydrocarbons with greater than 99% efficiency in an hour under 200 atm of CO_2 containing 10 atm of H_2 at 313 K using Pd/PDMS catalysts. The proposed Pd/PDMS catalysts can be reused without losing their activity and are significantly more active than commercial catalysts and a previously reported Pd nanoparticle catalyst stabilized in high-density polyethylene.

1. Introduction

Using supercritical carbon dioxide (sc-CO_2) as a solvent medium for chemical reactions offers several advantages compared to conventional organic solvents. These advantages include minimization of liquid waste generation, a high rate of mass transfer, and rapid separation of products. Particularly in catalytic hydrogenation, sc-CO_2 is superior to conventional solvents because hydrogen gas is completely miscible with sc-CO_2. Dispersion of catalysts in the fluid phase is a major issue affecting catalytic performance when processing heterogeneous catalytic reactions in sc-CO_2. However, the dispersion of conventional activated carbon or alumina-supported metal catalysts in sc-CO_2 is usually difficult to achieve, even with vigorous stirring. Therefore, selection of a suitable support for the dispersion of metal catalysts in the fluid phase is of great interest for catalytic hydrogenation in sc-CO_2.

Researchers have recently demonstrated that polymer-supported metal nanoparticles are highly efficient for heterogeneous catalysis in sc-CO_2 [1–6]. A major advantage of using this type of catalyst for sc-CO_2 reactions is that polymers tend to swell in sc-CO_2, allowing reactants to diffuse easily into the CO_2-swollen polymer and make contact with all embedded metal nanoparticles in the polymer matrix. As a result, the internal mass transfer resistance that usually exists in inorganic supports may be greatly reduced by polymer swelling. The degree of polymer swelling in sc-CO_2 usually depends on the CO_2 pressure and temperature, and the nature of the polymer [7]. Previous research has presented the solubilities of sc-CO_2 in commonly available polymers such as polyethylene, polypropylene, polyvinyl chloride, polytetrafluoroethylene, and polydimethylsiloxane (PDMS) [8–12]. Among these polymers, PDMS has shown a relatively high degree of swelling in sc-CO_2 [12]. Therefore, PDMS appears to be a desirable polymer to stabilize metallic nanoparticles for effective catalytic reactions in sc-CO_2.

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two classes of organic compounds of great concern in the environment. Developing effective and environmentally sustainable methods for the remediation of PAH- and PCB-contaminated materials is of considerable interest in environmental research. Researchers have developed a number of methods for degrading PCBs and PAHs, including chemical, biological, oxidation, and thermal techniques [13–20]. Among these methods,

the catalytic hydrodechlorination of PCBs and the hydrogenation of PAHs using noble metal catalysts have drawn significant attention due to their simplicity, high efficiency, and low energy consumption [21–30].

Certain reports show that metal nanoparticles can be immobilized on silica or in microfluid reactors fabricated from PDMS by surface adsorption [31,32]. This study proposes a method for synthesizing highly active and reusable palladium nanoparticles in PDMS (Pd/PDMS). This study evaluates the catalytic ability of Pd/PDMS catalysts through the catalytic hydrogenation of PAHs and hydrodechlorination of PCBs in sc-CO_2. Catalytic reactions in sc-CO_2 were investigated by *in situ* spectroscopic measurements using a high-pressure fiberoptic cell connected to a UV/Vis spectrometer with a charge-coupled device (CCD) array. The observed reaction rates of PAHs and PCBs for the Pd/PDMS catalysts in sc-CO_2 are significantly faster than those for commercial Pd catalysts supported on charcoal (Pd/C) and γ-alumina (Pd/Al_2O_3). The reaction rate is also faster than that previously reported for polyethylene-stabilized Pd nanoparticle catalysts (Pd/HDPE) for the hydrodechlorination of PCBs and the hydrogenation of PAHs in sc-CO_2. The superior performance of the Pd/PDMS catalyst can be attributed to a high degree of polymer swelling in sc-CO_2 and strong absorption of hydrophobic reactants by PDMS.

2. Experimental

2.1. Chemicals and reagents

Palladium hexafluoroacetylacetonate [Pd(hfa)$_2$] (97%) as a metal precursor was purchased from Aldrich (St. Louis, MO). Pd catalysts attached to conventional supports such as activated carbon (10 wt.%, catalog number: 205699) and Al_2O_3 (5 wt.%, catalog number: 205710) were also purchased from Aldrich (St. Louis, MO). The dispersion values and average diameter of metal particles of commercial Pd/C and Pd/Al_2O_3 appear in previous research [33,34]. Liquid carbon dioxide (>99.99%) and H_2 gas were supplied by Oxarc (Spokane, WA). HPLC grade hexane was purchased from Fisher Scientific (Fair Lawn, NJ) as a trap solution. Biphenyl, benzene, naphthalene, anthracene, phenanthrene, and pyrene were purchased from Aldrich (St. Louis, MO). 4-Chlorobiphenyl and 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101) were obtained from Ultra Scientific (North Kingstown, RI). A Sylgard-184 kit consisting of a silicone elastomer base and a curing agent was purchased from Dow Corning (Midland, MI) for PDMS synthesis.

2.2. Catalyst preparation

The Pd/PDMS catalyst was prepared as follows: Sylgard-184 silicone elastomer base (2.5 g), 14.8 mg of Pd(hfa)$_2$, and 15 mL of hexane were mixed in a crucible and sonicated for 10 min. When the solution became clear, 0.29 g of the curing agent was added to the solution and stirred at 313 K for 12 h. Reduction of Pd^{2+} in Pd(hfa)$_2$ within the PDMS polymer was subsequently performed under 20 atm of H_2 at 353 K for 1 h in a closed container. After reduction, the Pd/PDMS catalyst was cleaned under 100 atm of CO_2 with a flow rate of 1–2 mL/min at 353 K for 1 h. After cleaning, the resulting Pd/PDMS chunk was cut in small cubes (~9 mm^3) for catalytic hydrodechlorination of PCBs and hydrogenation of PAHs. A transmission electron microscope (TEM, Hitachi H-7100, Tokyo, Japan) operating at 80 kV was used to determine the size of the Pd nanoparticles in the PDMS support. The sample was prepared for TEM by slicing the Pd/PDMS catalysts into approximately 205 nm thin films with the diamond knife of a RMC MTXL Cryo-ultramicrotome at roughly −50 °C. All stock solutions were prepared by dissolving each chemical in hexane with a concentration

of approximately 0.1 M. X-ray photoelectron spectroscopy (XPS) experiments were performed on a Thermo K-Alpha electron spectrometer (Waltham, MA). Monochromatic radiation from an Al K-α X-ray source was used for excitation. The analyzer chamber was maintained at a base pressure of 5×10^{-9} mbar during the measurement. Energy dispersive X-ray spectroscopy (EDX) experiments were performed on a Hitachi S-3500H SEM (Tokyo, Japan).

2.3. Instruments and experimental procedure

This study used an sc-CO_2 system and experimental procedure presented in previous literature [35,36] for monitoring catalytic reactions using *in situ* UV/Vis absorption spectroscopy. The pressure and temperature of the system were controlled by an ISCO syringe pump (Model 260D, Lincoln, NB) with a series D pump controller and a Varian GC oven (Model 3700, Palo Alto, CA). This high pressure equipment composed of stainless steel material was purchased from High Pressure Equipment Company (HiP, Erie, PA). The experimental procedure is as follows: exactly 2.5 g of the Pd/PDMS catalyst was placed in a 20 mL reaction cell preheated to the desired temperature (313 K). For each experiment, 10 μL of PAH or PCB stock solution were added to a small glass beaker placed on top of the Pd/PDMS catalyst. After solvent evaporation, the reactor was closed and pressurized with 100 atm of CO_2. In a separate cell, 200 atm of a CO_2/H_2 mixture containing 10 atm of H_2 was premixed and subsequently introduced to the reaction cell via pressure difference. The reaction was monitored *in situ* by a UV/Vis spectrometer (Model SI-440, Spectral Instruments, Tucson, AZ) with a CCD array. Absorption spectra of the CO_2 phase were recorded between 200 and 350 nm every 5 s. After each reaction, the system was depressurized and the products were collected in a hexane trap solution for GC/MS (Shimadzu QP2010S equipped with SHRXI-5MS column) (Columbia, MD) analysis.

3. Results and discussion

3.1. Synthesis and characterization of the Pd/PDMS catalysts

Synthesis of the Pd/PDMS catalysts includes two major steps: (1) a polymerization process and (2) the reduction of Pd metal precursors embedded in the polymer matrix. For the polymerization step, Sylgard-184 silicone elastomer base, a curing agent, Pd(hfa)$_2$, and hexane were mixed in a crucible. The mass ratio of the silicone elastomer base to the curing agent was set at 8.6 for preparing PDMS polymers with the smallest crosslink degree that would result in the highest degree of swelling in sc-CO_2. A ratio less than 8.6 resulted in a higher crosslink degree, stiffening the PDMS polymer to be swollen by sc-CO_2. The polymerization temperature was set from 313 K to 373 K. At higher temperatures, the polymerization time was shorter, but small bubble voids formed affecting the distribution of Pd(hfa)$_2$ in the PDMS polymer. For this reason, 313 K was chosen for the polymerization process. Hexane was used as a solvent in the polymerization process to (1) mix Pd(hfa)$_2$ and PDMS homogeneously and (2) form a porous polymer after evaporating the solvent. After the polymerization step, the color of the PDMS polymer was yellow, indicating that Pd(hfa)$_2$ was well dispersed. The Pd^{2+} in Pd(hfa)$_2$ was reduced to zero-valance Pd metal by H_2 at 353 K. After H_2 reduction, the yellow PDMS polymer became black, indicating the formation of Pd nanoparticles. The concentration of Pd in the PDMS polymer was 0.12% by weight assuming that all added Pd(hfa)$_2$ was deposited in the PDMS polymer during the polymerization step. The size of the Pd particles in the PDMS was determined by transmission electron microscopy (TEM). The average size of the Pd particles in the PDMS support was 12.9 ± 7.5 nm based on 198 particle counts as shown in the TEM image in Fig. 1.
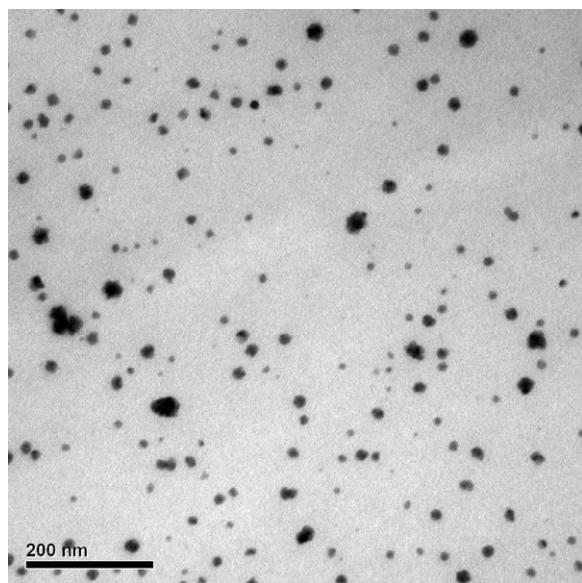
Fig. 1. TEM micrograph of the Pd/PDMS catalyst (Scale bars = 200 nm, average size of Pd particles = 12.9 ± 7.5 nm).

Fig. 3. XPS spectrum of the Pd/PDMS catalyst.

3.2. Catalytic hydrodechlorination of PCBs and hydrogenation of PAHs over Pd/PDMS catalysts in sc-CO_2

The catalytic ability of Pd/PDMS was first investigated through catalytic hydrogenation of biphenyl and catalytic hydrodechlorination of 4-chlorobiphenyl and PCB 101 in sc-CO_2. The same catalytic system was then applied to hydrogenation of benzene and PAHs including naphthalene, anthracene, phenanthrene, and pyrene. The amount of H_2 used in this study was much larger than that of reactants (over 100 times). The H_2 pressure in the system was assumed to remain constant during catalytic reactions. The conversion of reactants was determined by *in situ* UV/Vis absorption spectroscopic measurements in the CO_2 phase, and the distribution of products was measured by GC/MS analysis of the trap solution after the experiment. Fig. 5a shows the UV/Vis spectra of biphenyl recorded at different times during catalytic hydrogenation over Pd/PDMS in sc-CO_2 at 313 K. The arrow mark in Fig. 5a indicates the chosen absorption peak for biphenyl conversion measurements. The intensity of the absorption peak of biphenyl decreases with time, falling to less than 1/10 of the initial value in 6 min. Fig. 5b shows the absorption spectra for catalytic hydrodechlorination of 4-chlorobiphenyl in sc-CO_2 (PCB 101 has a similar absorption spectrum). This result is similar to the biphenyl result, i.e., the conversion is higher than 90% in 6 min. After 30 min of reaction time, biphenyl and two PCBs were nearly 99% converted to bicyclohexyl with a barely detectable amount (<1%) of cyclohexylbenzene as shown in Table 1. Fig. 5c–g show the

A histogram of the size distribution for the TEM image is shown in Fig. 2. The size distribution is as follows: 35% of Pd particles ranged between 2 and 10 nm, while 53% ranged between 11 and 20 nm. In this method, PDMS can disperse the metal nanoparticles efficiently. The presence of metallic Pd in the composite was confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX) (Figs. 3 and 4, respectively). In the XPS analysis, two contributions corresponding to different Pd species can be observed after deconvolution of the Pd 3d spectrum by the peakfit software. The binding energy (BE) of 3d3/2 at 340.6 eV and 3d5/2 at 335.3 eV is consistent with Pd metal, and the BE of 3d3/2 at 341.9 eV and 3d5/2 at 336.5 eV is consistent with the presence of an oxidized state [37–39]. The proportion of Pd and PdO is 68/32. These XPS results suggest that metallic Pd(0) is the predominant species in the Pd/PDMS catalyst. The EDX spectrum shows only Pd in the Si matrix. The Pt peaks in Fig. 4 represent the Pt present in the sample holder.
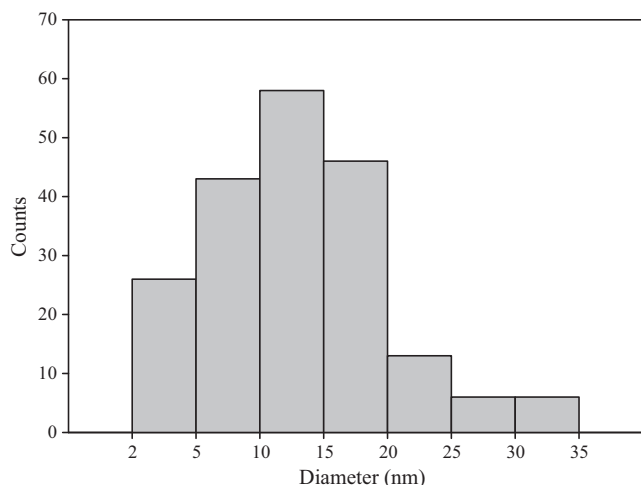

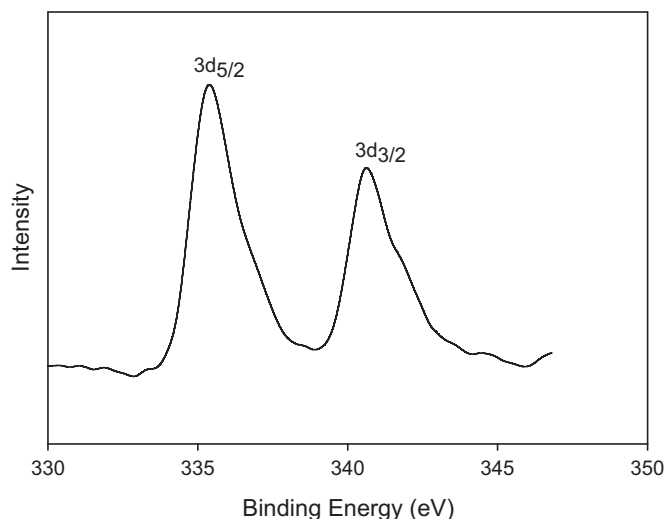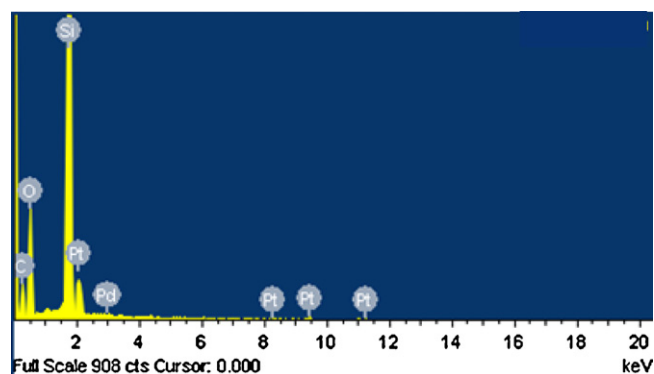**Fig. 2.** Histogram of the size distribution for TEM image.

Fig. 4. EDX spectrum of the Pd/PDMS catalyst. The Pt peak of the EDX spectrum comes from sample Pt coating for SEM/EDX.
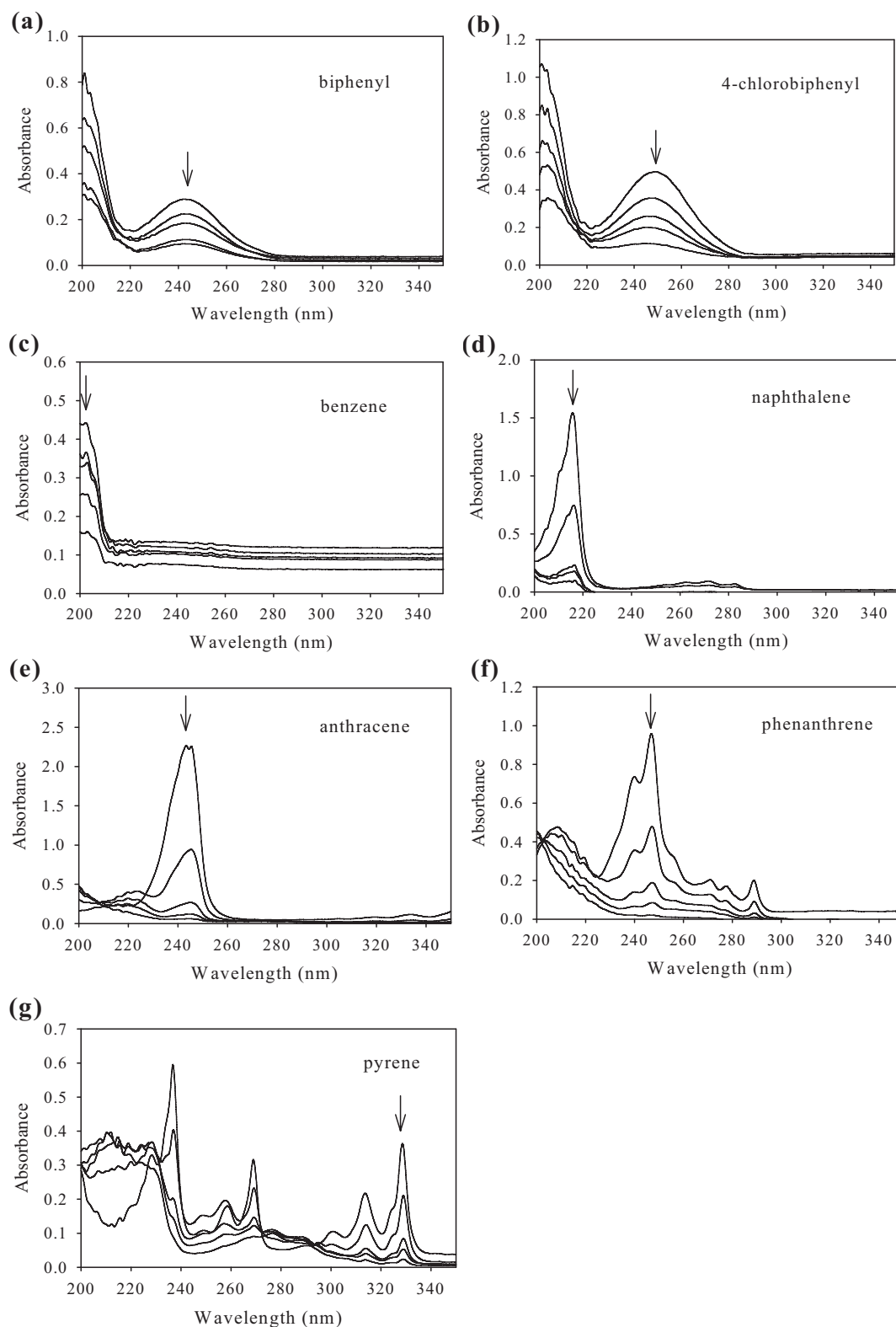
Fig. 5. Catalytic hydrodechlorination and hydrogenation of (a) biphenyl, (b) 4-chlorobiphenyl, (c) benzene, (d) naphthalene, (e) anthracene, (f) phenanthrene, and (g) pyrene over the Pd/PDMS catalyst in sc-CO$_2$. Conditions: 10^{-6} mol reactants, 313 K, 200 atm of CO$_2$ containing 10 atm of H$_2$. Reaction time for each curve from top to bottom is 0, 1, 2, 3, and 5 min.

absorption spectra for catalytic hydrogenation of benzene, naphthalene, anthracene, phenanthrene, and pyrene, respectively. The absorption spectra of benzene and each PAH also rapidly decreased, similar to those of biphenyl and PCBs. The intensities of the absorption peaks of benzene, naphthalene, anthracene, phenanthrene, and pyrene decreased with time, falling to less than 1/10 of the initial value in 27, 8, 3, 5, and 2 min, respectively. Benzene and PAHs were all 99% converted to their corresponding saturated polycyclic hydrocarbons with a very small amount (<1%) of partially saturated intermediates after 27–60 min as shown in Table 1.

These experimental results suggest that the conversion of the seven reactants (excluding benzene) is higher than 90% after 2–8 min, and all eight reactants were converted to their corresponding saturated products after 27–60 min.

The same compound (biphenyl) was used to test the catalytic activity of Pd/PDMS. Results show that the trend of decreasing UV absorbance for each reactant is almost the same. An sc-CO_2 cleaning step (50 mL of sc-CO_2 with a flow rate of 2.0 mL/min at 200 atm and 313 K) is necessary after each experiment to remove impurities from the catalyst surface to extend the lifetime of the catalyst. After cleaning, Pd/PDMS is ready for the next experiment. No complicated procedure is required. The catalytic activity of Pd/PDMS was checked using *in situ* UV/Vis spectra after more than 70 experiments. The rate of decreasing absorbance was similar to the rates shown in Table 1, indicating that the activity remained the same. According to the literature, a decrease in conversion is also observed with other PDMS supports. This may be because the catalytic metal particles are only physically adsorbed on the inner surface of the support and the fouling of catalyst surfaces may block the active sites of the support resulting in catalyst deactivation [13,14].

3.3. Comparison with noble metal catalysts for catalytic hydrogenation

3.3.1. Commercial noble metals supported on charcoal and γ-alumina

Previous research reports the liquid phase hydrodechlorination and hydrogenation of PCBs and PAHs over metal catalysts. Performing the same reactions over Pd/PDMS using organic solvents rather than sc-CO_2 reveals several disadvantages: (1) lower solubility of H_2, (2) a lower diffusion coefficient, and (3) the weaker swelling ability of organic solvents. Ghattas et al. used a Pd–Rh catalyst to detoxify chlorinated aromatic pollutants by completely removing the chlorine and the aromatic moieties to alicyclic rings under 80–100 °C and 27 atm of H_2 in 24 h in hexane or 1,2-$C_2H_4Cl_2$ [40].

Hiyoshi et al. reported the catalytic hydrogenation of biphenyl over commercially available charcoal-supported and γ-alumina-supported metal catalysts in sc-CO_2 (Pd/C, Pt/C, Ru/C, Rh/C, Pd/Al_2O_3, Pt/Al_2O_3, Ru/Al_2O_3, and Rh/Al_2O_3) [41]. According to this report, Rh/C has a higher conversion rate than do Pd/C and Pd/Al_2O_3 catalysts. The conversion results of Pd/C and Pd/Al_2O_3 catalysts are 0.7 and 1.3%, respectively, after 30 min reaction time and 6 MPa H_2 pressure. The same group also studied catalytic hydrogenation of naphthalene with commercial Pd/C, Pt/C, Ru/C, and Rh/C in sc-CO_2 [42]. The highest rate of conversion was 88.2% for Rh/C, and it was only 14.7% for Pd/C under 3 MPa H_2 pressure after 30 min. Using these commercial catalysts supported on charcoal and on γ-alumina in the proposed sc-CO_2 system suggested that the catalysts stayed on the bottom of the reaction cell without stirring. This was confirmed by visual observation through the window of a view cell. The dispersion of the catalysts in the fluid phase was not good, even under stirring. This poor dispersion makes it difficult to achieve a homogenous environment using commercial catalysts in this sc-CO_2 system. Therefore, reproducibility of catalytic hydrogenation reactions using commercial catalysts in sc-CO_2 is poor because the degree of catalyst dispersion is not consistent, even at the same stirring rate. One advantage of the Pd/PDMS catalyst is its relatively good dispersion of Pd nanoparticles in the sc-CO_2 reaction system. In the proposed catalytic system, the reaction cell is filled with the Pd/PDMS catalyst in which Pd nanoparticles are pre-dispersed in the PDMS polymer matrix. This arrangement is similar to a homogeneous catalysis environment. Consequently, each Pd nanoparticle can be brought into full play with respect to catalysis leading to high efficiencies in converting biphenyl and naphthalene to their corresponding saturated hydrocarbons in sc-CO_2. The Pd/PDMS catalyst described in this paper is highly efficient for converting PCBs and
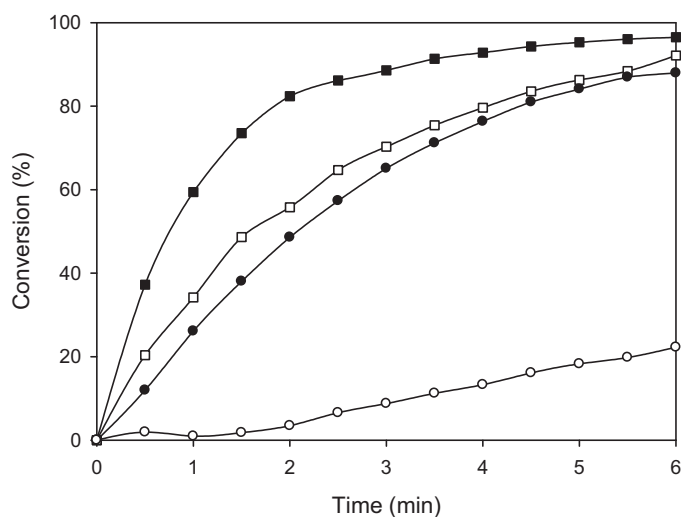

Fig. 6. The catalytic hydrodechlorination and hydrogenation of 4-chlorobiphenyl and phenanthracene in sc-CO_2 with Pd/PDMS and Pd/HDPE catalysts. Phenanthrene/PDMS (■); 4-chlorobiphenyl/PDMS (□); phenanthrene/HDPE (●); 4-chlorobiphenyl/HDPE (○). Conditions: 10^{-6} mol of reactants, 200 atm of CO_2 containing 10 atm of H_2, and 323 K.
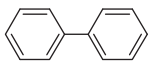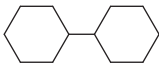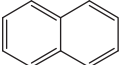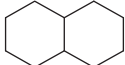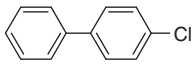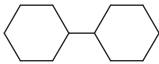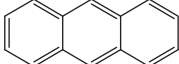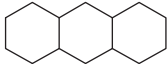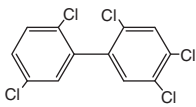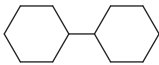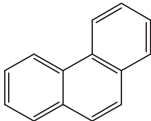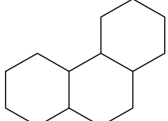
PAHs to saturated hydrocarbons by catalytic hydrodechlorination and hydrogenation under mild conditions in sc-CO_2.

3.3.2. Pd nanoparticles supported by high density polyethylene

Liao et al. studied the catalytic hydrodechlorination of PCBs using high density polyethylene stabilized Pd nanoparticles (Pd/HDPE) in sc-CO_2 [3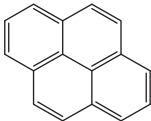5,36,43]. PCBs can be efficiently converted to bicyclohexyl via consecutive first-order reactions with biphenyl and cyclohexylbenzene as reaction intermediates. The principle of using the Pd/HDPE composite as a heterogeneous catalyst in sc-CO_2 is the same as the Pd/PDMS catalyst described in this paper. This study compares the catalytic activities of Pd/HDPE and Pd/PDMS via catalytic hydrogenation of phenanthrene and hydrodechlorination of 4-chlorobiphenyl in sc-CO_2 under the same experimental conditions. Fig. 6 shows the results. For the catalytic hydrogenation of phenanthrene, after 2 min, conversion using the Pd/PDMS catalyst is 30% higher than that using the Pd/HDPE catalyst. The difference in conversion between the Pd/PDMS and Pd/HDPE catalysts decreases over time (10% after 6 min). For the hydrodechlorination of 4-chlorobiphenyl, only 22% conversion was reached using the Pd/HDPE catalyst while over 90% conversion was achieved by the Pd/PDMS catalyst after 6 min. The catalytic activity of the Pd/PDMS catalyst is much greater than that of the Pd/HDPE catalyst in sc-CO_2 according to the experimental results. Since Pd nanoparticles in HDPE and in PDMS are all well dispersed in the reaction cell, the faster reaction rate for Pd/PDMS over Pd/HDPE may be attributed to (1) greater swelling of PDMS polymers in sc-CO_2 and (2) increased interaction between PDMS polymers and reactants.

Thurecht et al. measured the swelling ability of cross-linked PDMS and low-density polyethylene (LDPE) in sc-CO_2 using a high-pressure NMR technique [12]. Their NMR images show that the PDMS polymer exhibits a significant increase in volume, while the LDPE polymer exhibits negligible swelling under sc-CO_2 at 250 bar and 45 °C. The extent of PDMS polymer swelling in sc-CO_2 increases with increasing CO_2 pressure and decreasing crosslink density. For instance, the fraction of increase in volume can range from 0.2 to 0.5 when CO_2 pressure increases from 100 atm to 300 atm or the crosslink density of PDMS polymer changes from 2.82×10^{-4} to 6.04×10^{-5} mol/g. After swelling in sc-CO_2, the mobility of the polymer chains increases significantly, allowing easy diffusion of molecules in the polymer matrix. The PDMS polymer shows

Table 1
Catalytic hydrogenation of PCBs and PAHs using a Pd/PDMS catalyst in sc-CO_2.[a]

Reactant	Product distribution[b]	Reactant	Product distribution
Biphenyl	>99%	Naphthalene	>99%
4-Chlorobiphenyl	>99%	Anthracene	>99%
PCB 101	>99%	Phenanthrene	>99%
Benzene	>99%	Pyrene	>99%

[a] Conditions: 10^{-8} mol for benzene, 10^{-6} mol of other reactants; 2.5 g of Pd/PDMS catalyst; 200 atm of CO_2 containing 10 atm of H_2; 313 K; and 27–60 min.

[b] The minor product for biphenyl and each PCB is cyclohexylbenzene, while the minor product for benzene and each PAH is partially saturated polycyclic hydrocarbon from its corresponding PAH.

significantly superior swelling behavior in sc-CO_2 compared to the LDPE polymer. This results in easier diffusion of reactants in PDMS polymers during catalytic hydrogenation than in HDPE polymers, leading to a reduction of internal mass transfer resistance. PDMS polymers have been widely used as a common coating material in solid-phase microextraction (SPME) for solvent-free extraction of hydrophobic organic compounds. For example, Mayer et al. studied the absorption of 17 hydrophobic compounds including some PCBs and PAHs from the aqueous phase into solid-phase microextraction fibers coated with PDMS [44]. The partition coefficients for PCBs and PAHs between PDMS polymers and water ($K_{PDMS/water}$) generally increase with their hydrophobicity ($K_{PDMS/water} = 3 \times 10^3$ for phenanthrene and 2×10^5 for PCB 52; data for 4-chlorobiphenyl are unavailable) [44]. The strong interaction between PDMS and hydrophobic reactants likely facilitates the diffusion of reactants into the polymer matrix, resulting in a faster reaction rate for Pd/PDMS than for Pd/HDPE (Fig. 6).

Based on the discussion above, this study infers a reaction condition for the hydrodechlorination and hydrogenation of PCBs and PAHs catalyzed by a Pd/PDMS catalyst in sc-CO_2. Hydrophobic reactants such as PCBs or PAHs dissolved in a CO_2 phase are first absorbed into a PDMS phase, resembling a pre-concentration step. The reactants are easily diffused in the PDMS polymer with no significant internal mass transfer resistance due to the high degree of swelling in PDMS caused by the sc-CO_2. The reactants subsequently adsorb on the surface of Pd nanoparticles within the PDMS polymer matrix to undergo hydrogenation reactions with adsorbed hydrogen atoms in Pd, producing saturated hydrocarbons. Finally, the products diffuse away from the Pd/PDMS catalyst into the CO_2 phase. After a simple CO_2 cleaning process, the Pd/PDMS catalyst is ready for another catalytic cycle.

The detoxification of PAHs and PCBs to less toxic saturated polycyclic hydrocarbons can be achieved through Pd/PDMS-catalyzed hydrogenation in sc-CO_2 under milder conditions than those in conventional solvent systems; the process also generates less liquid waste. Although Pd metal is expensive, the Pd/PDMS catalyst is efficient and reusable. In addition, a continuous reaction system using heterogeneous catalysts in supercritical fluids has been proven feasible by some groups and has been tested for industrial applications [45,46].

4. Conclusions

Palladium nanoparticles supported by PDMS polymers are highly active in the catalytic hydrogenation of PAHs and hydrodechlorination of PCBs in sc-CO_2 under moderate conditions. The Pd/PDMS catalyst is easy to prepare and can be reused without losing activity even when used over 70 times. Reusability, an easy cleaning procedure, and mild reaction conditions are some of the advantages of the Pd/PDMS catalyst. The homogenous-like surrounding of Pd/PDMS catalysts in sc-CO_2, the high degree of swelling in PDMS polymers in sc-CO_2, and the strong interaction between PDMS and hydrophobic reactants may be responsible for the fast reaction rates observed in this study. This type of catalytic reaction system shows great potential for developing highly efficient and eco-friendly processes for the remediation of PAH- and PCB-contaminated materials in the environment.

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